

## Rutile-fluid trace element partitioning as an $fO_2$ indicator.

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Oxygen fugacity ( $fO_2$ ) is an important intensive variable which varies by ~6 orders of magnitude in modern tectonic settings [1], though its range in the Archean and Hadean lithosphere is not well constrained. Rutile offers one potential source of information; they form during fluid-rock interactions, can incorporate various redox-sensitive transition elements, can be U-Pb dated [2], and they are commonly found in Archean rocks and sediments. We present a new  $fO_2$  sensor wherein we quantify by experiment; rutile-fluid redox-sensitive trace element (TE) (V, Cr, Fe, Sn, Mo, etc.) partition coefficients (D) in a simple  $TiO_2$ - $H_2O$ -NaCl system. We use this information to explore the redox states of Archean metamorphic systems since the redox state of metamorphic fluids exerts control over ionic mobility and ore genesis. Experimental results reveal that rutile-fluid partition coefficients are a function of  $fO_2$  (~FMQ-4 to ~FMQ+10) and T (675 – 900 °C). While some elements show a positive relationship with  $fO_2$  (Cr, Fe, Sn), others show a negative one (V and Mo). In some cases, D-values vary over three orders of magnitude (V, Sn and Mo) across the range of oxygen fugacity explored here. The D vs  $fO_2$  relationship of any one of these TEs may be used to constrain the  $fO_2$  of formational environments of rutile. If the parent fluids cannot be measured, the ratio of these elements' concentrations in rutiles may be used to make a broad qualification of the  $fO_2$  of formational environments. We also measured these TEs along with Zr in natural detrital Archean rutiles (n=16) from metasediments of the Illara Greenstone Belt, Australia [3], which hosts Hadean zircons, and thus these rutiles might reveal information about the early Earth. Our rutiles have measurable amounts of our elements of interest ([Mo]  $\approx$  5 ppm, [Fe]  $\approx$  3000 ppm, etc.) and thus holds great potential for being subject to our  $[Mo/Fe]_{\text{rutile}}$ ,  $[V/Sn]_{\text{rutile}}$  and  $[Mo/Sn]_{\text{rutile}}$  vs  $fO_2$  calibrations to reveal the  $fO_2$  of their formational environment.

[1] Cottrell, E et al. (2021). <https://doi.org/10.1002/9781119473206.ch3> [2] Schmitt & Zack (2012), *Chem. Geol.* 332, 65. [3] Wyche et al., (2004), *Australian Journal of Earth Sciences* 51(1), 31.